

Landau Expansion for the Critical Point of a Polydisperse System

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The effect of polydispersity on the phase diagram of a simple binary mixture is to split the binodal curve into cloud and shadow curves that cross at the critical point (which, in general, is not at the maximum of either curve). Recent theories of polydispersity have shown, in favorable cases, how to project the (infinite-dimensional) free energy of the polydisperse system into a low dimensional space of ‘moment densities’. We address here the issue of how to construct a Landau expansion from the projected free energy. For the simplest case where the excess free energy depends on one moment density ρ_1 (this includes Flory Huggins theory for length-polydisperse chains) we show that the minimal expansion remains quartic in ρ_1 but nonetheless has seven independent coefficients, not two. When this expansion is handled correctly all the peculiar qualitative features of the polydisperse phase diagram are recovered, as are the slopes of the cloud and shadow curves, and the curvature of the cloud. However, to correctly predict the curvature of the shadow, certain fifth order terms must be retained. We also consider the phase diagram on the temperature-pressure plane, where the coexistence line broadens into a region. In general, the critical point lies between the point of maximum temperature and the point of maximum pressure on the perimeter of this region. This behavior is again captured by the Landau expansion.

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I. INTRODUCTION

Many systems, such as colloidal suspensions, and polymer blends and solutions, contain particles with an effectively continuous distributions of an attribute (σ , say) such as size, charge, or chemical character. Such systems are termed polydisperse [1]. Their phase equilibria can become complicated, but may exhibit relatively simple features including coexistence of two liquid phases of different composition. In some cases the tendency to phase separate is inherited from the underlying monodisperse physics (e.g. attractive colloids); in others it stems only from polydispersity (e.g. fractionation among chains with a spectrum of chemical compositions).

In a polydisperse system undergoing fluid-fluid demixing, the phase diagram looks rather different from that of a simple binary mixture even if the underlying physics is similar. It is common experimentally to draw the phase diagram on a composition/temperature plane; one effect of polydispersity is then to split the binodal curve into

cloud and shadow curves that cross at the critical point. (The latter is not at the maximum of either curve.) This is because, when a system is cooled to the point where it becomes globally unstable to phase separation (the cloud point), the incipient new phase (its shadow) differs from the old one not only in the number of particles per unit volume, as usual, but in its σ -distribution. Because of this difference, the incipient new phase does not itself represent a point on the cloud curve. (However, it does lie on the cloud curve of a *different system* whose overall size distribution coincides with that of the incipient, shadow phase).

An interesting question is whether all this behavior can be captured within a Landau expansion. There are at least two reasons to consider this. Firstly, conceptual (as well as practical) progress has been made recently in understanding phase equilibria in polydisperse systems within a certain class of mean-field models: those in which the excess free energy depends on the σ distribution only through a finite set of moments [1]. A promising method involves projecting the free energy onto a relatively small number of densities; when these are chosen correctly, the cloud, shadow, and spinodal curves, and with them any critical points, are found without approximation beyond those used to set up the mean-field free energy in the first place.

Due to their mean-field character and restricted set of relevant densities, such projection techniques should be reconcilable with a Landau expansion near the critical point – yet the unusual topology of the phase diagram appears, at first sight, to preclude this. In particular, the usual adoption of a quartic expansion in one density (with coefficients dependent only on temperature) is bound to exhibit a critical point at the apex of a binodal curve. We show below that a more careful Landau expansion does not suffer from this restriction, and instead reproduces the correct, more complicated behavior outlined above.

A second reason to study the Landau expansion is in the hope of going beyond mean field theory. Experimental values for the critical exponents of a polydisperse system [2] deviate from those of the monodisperse case and are consistent with Fisher-renormalised exponents [3]. However, to our knowledge, there is no explicit renormalization group calculation for a polydisperse system. Also, quite apart from calculating critical indices, it is important for many purposes (see e.g. [4]) to properly classify and identify the scaling fields near the critical

point, and this task cannot really be begun without a consistent description at the Landau level. Hence the Landau expansion presented below represents a first step towards a fuller understanding of polydisperse critical behavior beyond mean field level.

II. MONODISPERSE SYSTEM

In this section we review briefly the classical Landau expansion of the free energy around the critical point for a simple monodisperse system. This will facilitate a comparison with the polydisperse case and establish the notation.

In a canonical ensemble, the free energy \mathcal{F} is defined as a function of the temperature T , the number of particles N and the volume V . In the thermodynamic limit, however, we can define a reduced free energy (density) as

$$F(\rho, T) = \frac{\mathcal{F}(N, T, V)}{V k_B T}, \quad (1)$$

which is a function only of the density of particles $\rho = N/V$ and the temperature. At fixed temperature, any terms that are constant or linear in density are irrelevant for obtaining the phase equilibrium of the system (which is our main aim) since they can be assimilated into shifts of the entropy and of the chemical potential.

A. Critical Point

Within the mean field approximation, which is where the Landau expansion holds, the critical point must obey one condition common to all points on the spinodal curve,

$$\left. \frac{\partial^2 F}{\partial \rho^2} \right|_c = 0, \quad (2)$$

and a second condition particular to the critical point,

$$\left. \frac{\partial^3 F}{\partial \rho^3} \right|_c = 0, \quad (3)$$

where $|_c$ means evaluated at the critical point (ρ^c, T_c) .

B. Landau Expansion

Once the critical point is determined, the expansion follows as usual:

$$F(\rho, T) \approx \frac{1}{2} \left. \frac{\partial^2 F}{\partial \rho^2} \right|_{\rho^c, T} \delta \rho^2 + \frac{1}{3!} \left. \frac{\partial^3 F}{\partial \rho^3} \right|_{\rho^c, T} \delta \rho^3 + \frac{1}{4!} \left. \frac{\partial^4 F}{\partial \rho^4} \right|_{\rho^c, T} \delta \rho^4 + \dots, \quad (4)$$

where $\delta \rho \equiv \rho - \rho^c$. We forget about the constant and linear terms since, as described above, they can be viewed as (temperature dependent) shifts in the entropy and chemical potential with no effect on phase behavior.

The coefficients of the expansion depend on the temperature and can be expanded themselves about the critical temperature. Using Eqs. (2) and (3), and keeping the lowest order term for each coefficient, we obtain:

$$F(\rho, T) \approx \frac{1}{2} \left. \frac{\partial^2 F}{\partial \rho^2 \partial T} \right|_c \delta T \delta \rho^2 + \frac{1}{3!} \left. \frac{\partial^4 F}{\partial \rho^3 \partial T} \right|_c \delta T \delta \rho^3 + \frac{1}{4!} \left. \frac{\partial^4 F}{\partial \rho^4} \right|_c \delta \rho^4 + \dots, \quad (5)$$

where $\delta T \equiv T - T_c$. Since $\delta T \sim \delta \rho^2$ (see Eq. (7) below) the term in $\delta T \delta \rho^3$ is of higher order and can be neglected. Therefore, the lowest order expansion of the free energy has the simple form:

$$F(\rho, T) \approx A \delta T \delta \rho^2 + C \delta \rho^4, \quad (6)$$

for appropriate A and C . The coexisting phases obey the standard result

$$\delta T \approx -\frac{2C}{A} \delta \rho^2, \quad (7)$$

giving the well-known parabolic shape of the phase diagram around the critical point for monodisperse systems (always within the mean field approximation).

III. POLYDISPERSE SYSTEM

In the polydisperse case, the particles are not all identical but differ in certain scalar attributes (particle radius, charge, chain length...) which can be tagged with indices $\sigma_1, \sigma_2, \dots$. For simplicity, we focus on systems with just one polydisperse index σ , and write the corresponding density of particles as $\rho(\sigma)$. In this case, the free energy can be written as two parts, an ideal term and an excess term, as follows [5]:

$$F[\rho] = \int d\sigma \rho(\sigma) \{\log(\rho(\sigma)) - 1\} + F_{ex}[\rho]. \quad (8)$$

While the ideal part only depends on $\rho(\sigma)$ as shown, the excess part F_{ex} is, in general, an arbitrary functional of $\rho(\sigma)$ and a function of T . Here, in order to explore how polydispersity affects the Landau expansion around the critical point in a tractable manner, we restrict ourselves to cases where the functional dependence of the excess part of the free energy on the density distribution $\rho(\sigma)$ is through a single ‘generalized moment’ [6] of the distribution:

$$F[\rho] = \int d\sigma \rho(\sigma) \{\log(\rho(\sigma)) - 1\} + f(\rho_1, T), \quad (9)$$

where

$$\rho_1 = \int d\sigma \rho(\sigma) w_1(\sigma) \quad (10)$$

with $w_1(\sigma)$ an arbitrary weight function. Although this assumption seems restrictive, it is true for some important models including the Flory-Huggins theory of length-polydisperse polymer solutions and blends [6]. The models for which the excess part of the free energy depends on the density $\rho(\sigma)$ through a finite set of moments of this distribution, for which Eq. (9) is a particular example, are usually termed *truncatable* models.

A. The Parent Distribution Function

Polydispersity typically appears in the process of chemical manufacture of the particles of the system, so that the relative proportion of particles with different σ is fixed thereafter. The actual density of each species then depends on how much solvent is present. We define a parent distribution $P(\sigma)$ as

$$P(\sigma) = P_0 n(\sigma), \quad (11)$$

where $n(\sigma)$ is a normalized distribution (fixed by the initial preparation of the system) and P_0 is the overall density of particles, which varies as one moves along a ‘dilution line’ through the phase diagram. All other moments of the parent are fixed by P_0 ; for example,

$$P_1 = \int d\sigma P(\sigma) w_1(\sigma) = P_0 n_1 \quad (12)$$

where n_1 is fixed at synthesis via the parent:

$$n_1 = \int d\sigma n(\sigma) w_1(\sigma). \quad (13)$$

Although the parent distribution is globally fixed, the system can separate into coexisting phases with a distribution $\rho(\sigma)$ that is locally different from $P(\sigma)$. If there are two such phases α and β , with respective distributions $\rho^\alpha(\sigma)$ and $\rho^\beta(\sigma)$, the parent distribution is recovered as the volumetric average:

$$x^\alpha \rho^\alpha(\sigma) + x^\beta \rho^\beta(\sigma) = P(\sigma), \quad (14)$$

where Vx^α and Vx^β are the volumes of phases α and β , respectively. Note however that at a phase boundary which marks the onset of phase separation, the volume fraction of the incipient (shadow) phase is negligible and, therefore, the σ -distribution of the original (cloud) phase must coincide with the parent distribution.

B. Projection Method

Although for a given $n(\sigma)$ we require only one density (such as ρ_1), alongside temperature, to specify a point on

the phase diagram, the corresponding free energy must depend on the full density distribution $\rho(\sigma) = P_0 n(\sigma)$. Accordingly it is not correct to substitute the parent distribution in a functional like Eq. (9) to obtain a one-variable free energy $F(P_0)$ (or equivalently, $F(\rho_1)$). In fact such a substitution would describe a case where the normalized distribution $n(\sigma)$ were constrained to be equal in all coexisting phases – which is not the physical situation. Instead, in the case of Eq. (9), the equality of chemical potentials dictates that the σ -distribution of any cloud phase (which coexists, by definition, with an unperturbed parent) must obey

$$\rho(\sigma) = P(\sigma) e^{\lambda w_1(\sigma)}, \quad (15)$$

for an appropriate value of λ . This distribution is not proportional to the parent unless $\lambda = 0$ (when the phases are identical).

However, under certain conditions there is a procedure to transform the free energy functional into an effective free energy *function*. The conditions are first that (as in Eq. (9)) the excess free energy f only depends on the distribution $\rho(\sigma)$ through a finite set of moments (defined as in Eq. (10)); and second that we are only interested in phase boundaries (the cloud and the shadow curves) and the spinodals. The procedure, called the projection method [6,1], involves several steps briefly described here, and leads to a free energy function dependent only on the moments required to specify the excess free energy.

First, considers the free energy

$$F[\rho] = \int d\sigma \rho(\sigma) \left\{ \log \left(\frac{\rho(\sigma)}{P(\sigma)} \right) - 1 \right\} + f(\rho_1, T), \quad (16)$$

which, for our purposes, is equivalent to Eq. (9), since the inclusion of the parent as a denominator in the logarithm represents a linear term (which can be considered as a mere shift of the chemical potentials). But note that, for that equivalence to hold, the parent $P(\sigma)$, including P_0 , must be kept fixed as the density distribution $\rho(\sigma)$ varies: this observation is crucial to the Landau expansion developed below.

The projection method follows by minimising the first (ideal) term of this free energy subject to the constraint of fixed values for the moment(s) upon which the excess free energy depends. (The only such moment is ρ_1 in our case.) This yields

$$\rho(\sigma) = P(\sigma) e^{\lambda_1 w_1(\sigma)}, \quad (17)$$

where λ_1 is the Lagrange multiplier used to constrain the minimization, determined by ρ_1 through

$$\rho_1 = \int d\sigma P(\sigma) w_1(\sigma) e^{\lambda_1 w_1(\sigma)}. \quad (18)$$

Since both the parent phase (the cloud) and the coexisting phase (the shadow, Eq. (15)) obey Eq. (17) for different values of λ_1 , the method contains no approximation

when it comes to finding the phase boundaries. However, if the σ -distribution of any of the phases adopts a form different from (17), the method produces only approximate results. This occurs whenever the system separates into finite volumes of more than one phase, that is, everywhere *within* the cloud curve. (In Eq. (14), the projection method is inexact when x_α and x_β are both nonzero.)

The free energy obtained by this method is [6]

$$F(\rho_1, T) = \lambda_1 \rho_1 - \rho_0 + f(\rho_1, T), \quad (19)$$

where

$$\rho_0 = \int d\sigma P(\sigma) e^{\lambda_1 w_1(\sigma)}. \quad (20)$$

This free energy depends on only one density variable, since both λ_1 and ρ_0 are given by ρ_1 . The coexisting phases are obtained from this free energy *function* via the common tangent method, as in the monodisperse case.

C. Dilution Line

As mentioned above, the projected free energy requires knowledge of the parent distribution function $P(\sigma)$, whose normalization P_0 varies as one moves along a dilution line on the phase diagram. For this reason, the projected free energy $F(\rho_1, T)$ depends parametrically on P_0 , through $\lambda_1(\rho_1, P_0)$ and $\rho_0(\lambda_1, P_0)$; see Eqs. (18) and (20), respectively. This dependence is parametric because, in the process of calculating the coexistence between phases, P_0 must remain fixed, so as to maintain the equivalence of Eq. (9) and (16).

Suppose that, for fixed P_0 and T , we obtain by this method a coexistence between phases α and β , with moment densities ρ_1^α and ρ_1^β , respectively. This determines the value of λ_1^α , λ_1^β , ρ_0^α , and ρ_0^β through Eqs. (18) and (20) which, in turn, determines the density distribution of the two phases $\rho^\alpha(\sigma)$ and $\rho^\beta(\sigma)$ via Eq. (17). In general, neither of these distributions is the parent distribution.

This is consistent with the fact that the parent distribution does not coexist with a second phase for arbitrary combinations of P_0 and T ; this happens only on the cloud curve. To find the cloud curve, we combine the coexistence conditions derived above with the equation of the dilution line, so that one of the coexisting phases (α say) is the parent distribution; this implies that $\rho^\alpha(\sigma) = P(\sigma)$, $\lambda_1^\alpha = 0$, $\rho_0^\alpha = P_0$, and $\rho_1^\alpha = P_0 n_1$ (or $\rho_1^\alpha = \rho_0^\alpha n_1$).

D. Critical Point

The critical point of the polydisperse system lies at the intersection of the cloud and shadow curves and is, therefore, correctly described (given Eq. (9)) by the projected free energy. The equations to determine it are analogous to those of the monodisperse case,

$$\left. \frac{\partial^2 F}{\partial \rho_1^2} \right|_c = 0 \quad (21)$$

and

$$\left. \frac{\partial^3 F}{\partial \rho_1^3} \right|_c = 0, \quad (22)$$

where $|_c$ means evaluated at the critical point $(\rho_1^c, T_c; P_0^c)$. Note that these two equations have three unknowns, namely ρ_1^c , T_c and P_0^c , and must be complemented by the dilution line constraint, $\rho_1^c = P_0^c n_1$.

IV. LANDAU EXPANSION

The projected free energy $F(\rho_1, T; P_0)$ can now be expanded about the critical point,

$$F \approx \frac{1}{2} \left. \frac{\partial^2 F}{\partial \rho_1^2} \right|_{\rho_1^c, T; P_0} \delta \rho^2 + \frac{1}{3!} \left. \frac{\partial^3 F}{\partial \rho_1^3} \right|_{\rho_1^c, T; P_0} \delta \rho^3 + \frac{1}{4!} \left. \frac{\partial^4 F}{\partial \rho_1^4} \right|_{\rho_1^c, T; P_0} \delta \rho^4 + \dots, \quad (23)$$

where $\delta \rho \equiv \rho_1 - \rho_1^c$. As before, the constant and linear terms have been dismissed.

Now we must expand the coefficients of this expansion around the critical values not only of T , as we did in the monodisperse case, but also of P_0 . One might think that, after doing this, the free energy could be written, to the lowest order, as

$$F \approx (A_1 \delta T + A_2 \delta P_0) \delta \rho^2 + C \delta \rho^4, \quad (24)$$

where $\delta P_0 \equiv P_0 - P_0^c$. If so, the term in brackets should be of order $\delta \rho^2$ to balance the term of order $\delta \rho^4$. However, the second term in the brackets is actually linear in $\delta \rho$, as dictated by the dilution line $\delta P_0 = \delta \rho / n_1$. These two facts can only be obeyed if the first term in the brackets behaves like $A_1 \delta T \approx -A_2 \delta \rho / n_1 + \mathcal{O}(\delta \rho^2)$ (instead of $\delta T \sim \delta \rho^2$, as in the monodisperse case). This corresponds to the fact that, generically, the critical point is no longer at the top of the coexistence curve. Therefore, to maintain consistently the order of the approximation, the correct lowest order expansion of the free energy must contain all terms of order $\delta \rho^4$:

$$F \approx \frac{1}{2} \left[\left. \frac{\partial^3 F}{\partial \rho_1^3 \partial T} \right|_c \delta T + \left. \frac{\partial^3 F}{\partial \rho_1^3 \partial P_0} \right|_c \delta P_0 + \frac{1}{2} \left. \frac{\partial^4 F}{\partial \rho_1^4 \partial T^2} \right|_c \delta T^2 + \frac{1}{2} \left. \frac{\partial^4 F}{\partial \rho_1^2 \partial P_0^2} \right|_c \delta P_0^2 + \left. \frac{\partial^4 F}{\partial \rho_1^2 \partial T \partial P_0} \right|_c \delta T \delta P_0 \right] \delta \rho^2 + \frac{1}{3!} \left[\left. \frac{\partial^4 F}{\partial \rho_1^4 \partial T} \right|_c \delta T + \left. \frac{\partial^4 F}{\partial \rho_1^4 \partial P_0} \right|_c \delta P_0 \right] \delta \rho^3 + \frac{1}{4!} \left. \frac{\partial^4 F}{\partial \rho_1^4} \right|_c \delta \rho^4 + \dots \quad (25)$$

To continue, let us define the functions

$$\rho_m = \int d\sigma P(\sigma) (w_1(\sigma))^m e^{\lambda_1 w_1(\sigma)}, \quad (26)$$

for any $m = 0, 1, 2, \dots$, which are an expanded set of generalised moments consistent with the previous definitions Eq. (18) and (20). These functions depend on ρ_1 and P_0 and, indeed, they obey:

$$\frac{\partial \rho_m}{\partial \rho_1} = \frac{\rho_{m+1}}{\rho_2}, \quad (27)$$

and

$$\frac{\partial \rho_m}{\partial P_0} = \frac{1}{P_0} \left(\rho_m - \frac{\rho_1 \rho_{m+1}}{\rho_2} \right). \quad (28)$$

Very importantly, these equations imply that the derivatives of any (generalised) moment with respect to ρ_1 gives rise to functions of moments (Eq. (27)), and the derivatives of any moment with respect to P_0 must vanish in the monodisperse limit (as does Eq. (28)).

With these definitions, we can write the second derivative of the free energy, from which all the coefficients of the expansion (25) can be obtained, as:

$$\frac{\partial^2 F}{\partial \rho_1^2} = \frac{1}{\rho_2} + \frac{\partial^2 f(\rho_1, T)}{\partial \rho_1^2}. \quad (29)$$

Now note that, since T and P_0 appear in disjunct parts of the free energy (as in the original free energy, Eq. (19)), all crossed terms must vanish:

$$\frac{\partial^2 F}{\partial T \partial P_0} = 0. \quad (30)$$

Accordingly, the coefficients of the expansion can be divided into three different groups: those including only derivatives with respect to ρ_1 , those including derivatives with respect to T , and those including derivatives with respect to P_0 . While the first group of coefficients originates from the full free energy, the second originates from the excess part of the free energy ('the interactions'), and the third group arises from the ideal part of the free energy ('the entropy'). These three groups of coefficients have a distinct dependence on polydispersity. In particular, all the coefficients stemming from the ideal part (those multiplying any power of δP_0) must vanish in the monodisperse limit [7], hence recovering the ordinary Landau expansion, Eq. (6) (plus some terms e.g. in $\delta T^2 \delta \rho^2$ that are higher order corrections in this limit).

In brief, the correct lowest order expansion of the free energy, retaining all terms to fourth order in density, is therefore

$$F \approx (A_1 \delta T + A_2 \delta P_0 + A_3 \delta T^2 + A_4 \delta P_0^2) \delta \rho^2 + (B_1 \delta T + B_2 \delta P_0) \delta \rho^3 + C_0 \delta \rho^4, \quad (31)$$

where the coefficients of terms involving δT (those with odd indices: A_1, A_3 and B_1) only depend on derivatives of the excess free energy f , and the coefficients of terms

involving δP_0 (A_2, A_4 and B_2) stem solely from the ideal entropy term of the system and not the interactions. The latter vanish in the monodisperse limit; for example,

$$A_2 \equiv \frac{1}{2 P_0^2} \left(\frac{n_1 n_3}{n_2^3} - \frac{1}{n_2} \right), \quad (32)$$

where $n_1, n_2 \dots$ are generalized moments of the (normalized) parent distribution,

$$n_m \equiv \int d\sigma n(\sigma) (w_1(\sigma))^m, \quad (33)$$

which do not depend on any thermodynamic variable.

It is interesting to point out here that the ultimate reason why the critical point is not on the top of the cloud curve is that the squared term of the free energy expansion at the critical point behaves effectively as $\delta T^2 \delta \rho^2$ instead of the usual $\delta T \delta \rho^2$.

We stress that although the coefficients A_2, A_4 and B_2 are small for narrow polydispersities, the expansion (31) is asymptotically exact around the critical point for arbitrary (not necessarily narrow) polydisperse distributions. As ever, 'exact' means exact within a mean-field free energy of the form Eq. (9).

A. Cloud Curve

In order to obtain an expression for the cloud curve, we can write the free energy expansion (31) in terms of a *shifted* density

$$\delta \eta \equiv \delta \rho + \frac{B_1 \delta T + B_2 \delta P_0}{4 C_0}, \quad (34)$$

obtaining an asymptotic expression of the form

$$F \approx A \delta \eta^2 + C_0 \delta \eta^4, \quad (35)$$

where

$$A \equiv A_1 \delta T + A_2 \delta P_0 + A_3 \delta T^2 + A_4 \delta P_0^2 - \frac{3 (B_1 \delta T + B_2 \delta P_0)^2}{8 C_0}. \quad (36)$$

Starting from this simple expression, the coexisting states follow immediately as

$$\delta \eta \approx \pm \sqrt{-\frac{A}{2 C_0}}. \quad (37)$$

These two coexisting densities correspond to distribution functions given by Eq. (17), neither of which is in general the parent distribution function $P(\sigma)$. In order to obtain the appropriate cloud curve, we must therefore impose the dilution line constraint, $\delta \rho^{CL} = n_1 \delta P_0$, which leads to the following expression for the cloud curve:

$$\delta T_{CL} \approx \alpha_{CL} \delta \rho + \beta_{CL} \delta \rho^2 + \mathcal{O}(\delta \rho^3), \quad (38)$$

where the slope of the cloud curve at the critical point is given by

$$\alpha_{CL} \equiv -\frac{A_2}{A_1 n_1}, \quad (39)$$

and its curvature by

$$\beta_{CL} \equiv \frac{C_0}{A_1} \left[(1 - \Delta)^2 - 3 \right] - \frac{A_4}{A_1 n_1^2} - \frac{A_2^2 A_3}{A_1^3 n_1^2}, \quad (40)$$

where

$$\Delta \equiv \frac{A_1 B_2 - A_2 B_1}{2 A_1 C_0 n_1}. \quad (41)$$

As predicted (preceding Eq. (25) above), we have thus established that $A_1 \delta T + A_2 \delta P_0 \sim \delta \rho^2$, with exact cancellation of the terms linear in $\delta \rho$. This shows the consistency of the approximation and proves that none of the terms in Eq. (25) can be discarded in the expansion.

One consequence of these results concerns the geometric location of the critical point along the cloud curve. For the critical point to remain at the apex of the cloud curve (which is where it resides in the monodisperse limit), the slope of the cloud curve at the critical point α_{CL} , Eq. (39), must vanish; this requires $A_2 = 0$. According to Eq. (32), this requires very particular combinations of the parent distribution and weight function $w_1(\sigma)$. If the latter only adopts positive values, A_2 is strictly positive except in the monodisperse limit so that the critical point will move away from the top of the cloud curve even for infinitesimal polydispersity [8]. Since the argument originates from the entropic part of the free energy, it may hold more generally than for systems obeying Eq. (9) [9,10].

For monodisperse systems, the slope α_{CL} vanishes, while β_{CL} tends to $-2C_0/A_1$, thus recovering the classical scenario that leads to Eq. (7): the cloud curve forms the binodal curve with a quadratic maximum where the critical point resides.

B. Shadow Curve

The shadow curve does not, of course, obey the dilution line constraint, and therefore is not obtainable directly from Eq. (37). Nonetheless we expect

$$\delta T_{SH} \approx \alpha_{SH} \delta \rho + \beta_{SH} \delta \rho^2 + \mathcal{O}(\delta \rho^3). \quad (42)$$

To find α_{SH} , we may use Eq. (37) to write a relation between the cloud and the shadow curves,

$$\delta \eta^{CL} + \delta \eta^{SH} \approx 0. \quad (43)$$

This yields, upon substitution of Eq. (34),

$$\alpha_{SH} \equiv -\frac{\alpha_{CL}}{1 + \Delta}. \quad (44)$$

Interestingly though, Eq. (43) does not provide the correct curvature of the shadow curve, β_{SH} , as can easily be checked numerically for the example considered below (Section V). This is because the curvature of the shadow in fact depends on some higher-order terms (of order $\delta \rho^5$) that were not included in Eq. (31). The fifth-order terms are

$$\Delta F = (A_5 \delta T^3 + A_6 \delta P_0^3) \delta \rho^2 + (B_3 \delta T^2 + B_4 \delta P_0^2) \delta \rho^3 + (C_1 \delta T + C_2 \delta P_0) \delta \rho^4 + D_0 \delta \rho^5, \quad (45)$$

Including these (fifth-order) terms in the expansion, Eq. (31), transforms Eq. (43) into

$$\delta \eta^{CL} + \delta \eta^{SH} \approx \frac{(A_1 \delta T + A_2 \delta P_0 + A_3 \delta T^2 + A_4 \delta P_0^2) D_0}{2 (C_0 + C_1 \delta T + C_2 \delta P_0)^2} + \mathcal{O}(\delta \eta^3), \quad (46)$$

from which we finally obtain the expression

$$\beta_{SH} \equiv \frac{1}{(1 + \Delta)^3} \left[\beta_{CL} \left(1 + \frac{1}{2 C_0^2 n_1} (B_2 C_0 - A_2 D_0) \right) + \frac{\alpha_{CL}}{2 C_0^2 n_1^2} (B_2 C_2 - B_4 C_0 + A_4 D_0) + \frac{\alpha_{CL}^2}{2 C_0^2 n_1} (B_1 C_2 + B_2 C_1) + \frac{\alpha_{CL}^3}{2 C_0^2} (B_1 C_1 - B_3 C_0 + A_3 D_0) \right]. \quad (47)$$

In the monodisperse limit, analogously to the cloud curve, the slope α_{SH} vanishes and β_{SH} tends to $-2C_0/A_1$, thus forming the binodal curve by the merger of cloud and shadow.

C. Consequences of the Expansion

Note the progression in complexity of the coefficients needed in the expansion to compute the slopes, and then curvatures, of the cloud and shadow at the critical point. The slope of the cloud curve α_{CL} depends on just two coefficients of the expansion (A_1 and A_2); the slope of the shadow involves three extra coefficients (B_1 , B_2 and C_0); the curvature of the cloud at the critical point requires knowledge of all seven coefficients of the quartic Landau expansion, Eq. (31); that of the shadow also involves a selection of the fifth order terms (but not all of them): Table 1 shows which terms in the Landau expansion must be retained to correctly predict each of these parameters.

Although these results are obtained for a one-moment free-energy, Eq. (9), they involve higher moments of the parent distribution [6], as detailed in Table 1. Note also that the critical point and the spinodals depend only on a reduced set of moments; this holds to all orders in the Landau expansion. In contrast, order by order, the cloud and shadow curves involve progressively all the moments of the parent distribution, through Eqs. (27) and (28).

The results given above were obtained by the projection method, but since this gives the exact cloud and shadow curves, any other method for finding α_{CL} , β_{CL} ... within mean field theory must produce, necessarily, expressions equivalent to Eqs. (39,40,44,47).

D. Phase Diagram in Temperature-Pressure Plane

In the monodisperse case, the phase equilibria show up in the T - p phase diagram as a line of coexistence, ending at the critical point. If polydispersity is included, this line now broadens and adopts a banana-like shape of finite area, containing the values of temperature and pressure for which the system undergoes phase separation. In this case, the critical point appears on the perimeter of the coexistence region.

We now can calculate the shape of the coexistence region to the same order of approximation as we did with the cloud and the shadow. After projection of the free energy to give Eq. (19), the pressure of the system can be written in the familiar form [6]

$$\frac{p}{k_B T} = \frac{\partial F}{\partial \rho_1} \rho_1 - F, \quad (48)$$

which allows us to expand $\delta p \equiv p - p_c$ as

$$\frac{\delta p}{k_B T} \approx a_1 \delta T + a_2 \delta P_0 + b_1 \delta T^2 + b_2 \delta P_0^2 + \dots \quad (49)$$

where (just as occurred in Eq. (31)) the coefficients of terms involving δT (those with odd indices: a_1 and b_1) only depend on derivatives of the excess free energy f , and the coefficients of terms involving δP_0 (a_2 and b_2) derive solely from the ideal entropy of the system (not the interactions) and vanish in the monodisperse limit. For instance,

$$a_2 \equiv \frac{n_1^2}{n_2} - 1 \quad (\leq 0). \quad (50)$$

Substitution of the approximation derived in Section IV A for the cloud curve yields

$$\frac{\delta p}{k_B T} \approx \alpha_P \delta \rho + \beta_P \delta \rho^2, \quad (51)$$

where

$$\alpha_P \equiv a_1 \alpha_{CL} + \frac{a_2}{n_1} \quad (52)$$

and

$$\beta_P \equiv a_1 \beta_{CL} + b_1 \alpha_{CL}^2 + \frac{b_2}{n_1^2}. \quad (53)$$

A generic consequence of these results concerns the location of the critical point along the perimeter of the coexistence region on the T - P phase diagram. It is

clear on geometrical grounds that the critical point cannot be located at the point of maximum temperature and maximum pressure simultaneously, unless the coexistence region shows a kink at that point. Such a kink is not predicted by the Landau expansion, which gives smooth behavior everywhere; nor have we seen evidence for it in any of the models (or experiments) studied to date. Assuming these two turning points are indeed distinct, one can ask whether the critical point generically lies at one, at the other, or neither. We argued already above that generically, for systems obeying Eq. (9), the critical point is not at the maximum of T since this would require A_2 to vanish (Eq. 32). Likewise, for it to lie at the pressure maximum would require $\alpha_P = 0$ in Eq. (52), for which a fine tuning of the parameters appears necessary [11,10]. We conclude that generically it lies at neither of these points; indeed, as shown in the following example, it lies between them.

V. EXAMPLE

In this Section, we illustrate the results of the Landau expansion for the cloud and shadow curves of a particular system: an incompressible blend of two homopolymers. One of the polymers is considered polydisperse in length, with number densities $\rho(\sigma)$ where σ is the number of monomers on a chain (effectively a continuous parameter). The other polymer (or solvent) is monodisperse and has N' monomers. For this system, the free energy can be easily obtained from the Flory-Huggins theory and recovers the form (9). Specifically, the excess free energy reads [6]

$$f(\rho_1, \chi) = \frac{1 - \rho_1}{N'} \log \left(\frac{1 - \rho_1}{N'} \right) + \chi \rho_1 (1 - \rho_1), \quad (54)$$

where χ is the Flory parameter, which plays the role of an inverse temperature. The weight function for the moment ρ_1 is $w_1(\sigma) = \sigma$ (in the usual polymer jargon, ρ_1 is the monomer volume fraction ϕ).

As a normalised parent, we consider in this example a uniform distribution

$$n(\sigma) = \begin{cases} \frac{1}{2\sqrt{3}\Delta N} & \text{if } |\sigma - N| \leq \sqrt{3}\Delta N \\ 0 & \text{otherwise} \end{cases} \quad (55)$$

where $N = n_1 = \langle \sigma \rangle$ is the mean polymer size, and $\Delta N = (\langle \sigma^2 \rangle - \langle \sigma \rangle^2)^{1/2}$ is the standard deviation.

We plot in Figures 1 and 2 the resulting behavior for the case where the polymer solvent has $N' = 10$ monomers and the distribution of sizes of the solute follows Eq. (55) with $N = 1000$ and $\Delta N/N = 0.2$. (This corresponds, in polymer jargon, to a polydispersity index $M_w/M_n = \langle \sigma^2 \rangle / \langle \sigma \rangle^2 = 1.4$.)

We see from these plots that the Landau expansion, Eq. (31), captures correctly all the essential features of

the full mean-field model near the critical region, just as it does for monodisperse systems. In this example, the Landau predictions cross the cloud and shadow curves at the critical point (although the slopes and curvatures are correct). This behavior is inherited from the monodisperse case, and is presumably connected with an error in the third derivative of these curves.

Given the increased complexity of the phase behavior (separation of cloud and shadow curves; critical point not at the maximum of these; finite width coexistence region on the $p-T$ plot collapsing to a line in the monodisperse limit), we find this somewhat remarkable. We emphasize that every term in Eq. (31) must be retained to achieve this degree of consistency – and in particular to reproduce the correct curvature of the cloud; to get the curvature of the shadow also correct, one needs as well the higher terms in Eq. (45). The latter were included in the figure although leaving them out gives a result that, for this example, is only slightly less accurate. Despite all the extra complexity, the region of the phase diagram within which the Landau expansion could tolerably be used to replace the full calculation is similar to the monodisperse case.

VI. CONCLUSIONS

Within the one-moment form of the excess free energy represented by Eq. (9), we have derived a generalized Landau expansion, Eqs. (31,45), from which the characteristic features of polydisperse binary fluid coexistence can all be shown to follow. This Landau expansion was compared with direct calculation from the underlying (mean-field) free energy in a specific example (Figures 1 and 2) with excellent agreement near the critical point and qualitative agreement away from it. Note that truncation of the Landau expansion at the quartic order (Eq.31) may prove adequate for qualitative purposes if the curvature of the shadow is not important.

Our expansion is correct around the critical point for arbitrary polydispersity, be it broad or narrow. The monodisperse limit is recovered by decreasing the polydispersity. In a pressure-temperature representation this limit is highly singular: for example the slope of the perimeter of the coexistence region at the critical point will converge, as the monodisperse limit is taken, to a negative value – even though the coexistence line (onto which the region itself collapses in this limit) has positive slope everywhere! This behavior is easily understood from Figure 2, and the Landau expansion seems to have no difficulty dealing with it.

The perturbation series in density that underlies the Landau expansion contrasts with, and is complementary to, a previous perturbative approach that was developed for the limit of narrow polydisperse distributions [12]. The latter approach always breaks down close enough to the critical point (even within mean field theory, to

which, unlike our work, it is not limited in principle).

Finally, we note that although our Landau expansion was derived within the specific context of Eq. (9), the generic features of the phase diagram that it reproduces are seen rather generally in experiments and other theoretical models. We have not attempted explicit calculation for the case where more than one moment is present in the excess free energy, but since the topology of the phase diagram (near the fluid-fluid critical point) is already captured by Eq. (9), it is possible that any such refinements will not alter the basic structure of these results. A firm conclusion on this point is, however, left to future work.

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$$\frac{\partial^i}{\partial P_0^i} \frac{\partial^j}{\partial \rho_1^j} \left(\frac{1}{\rho_2} \right) \quad (56)$$

for appropriate $i \geq 1$ and $j \geq 0$ ($j=0$ means no derivative). The first j derivatives produce a certain function of moments (via Eq. (27)), while the following i derivatives produce terms vanishing in the monodisperse limit (via Eq. (28)).

- [8] Since, for any (not infinitely narrow) distribution, $n_1 n_3 - n_2^2 = \frac{1}{2} \int d\sigma d\sigma' n(\sigma) n(\sigma') w_1(\sigma) w_1(\sigma') (w_1(\sigma) - w_1(\sigma'))^2$, is necessarily positive if $w_1(\sigma)$ is.
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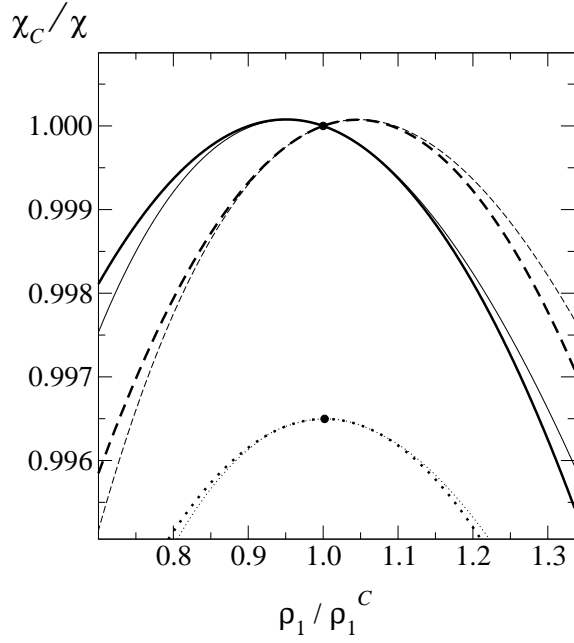


FIG. 1. Cloud (continuous) and shadow (dashed) curves of the polymeric system described in the text. The monodisperse limit, $\Delta N \rightarrow 0$, for which cloud and shadow curves merge into a single curve (the binodal), is also plotted as a dotted line. The thin lines represent the exact numerical solution of the model, while the thick lines represent the Landau expansion, which shows exact first and second order derivatives at the critical point. In the monodisperse case, the critical point rests at the top of the curve.

p/p_c

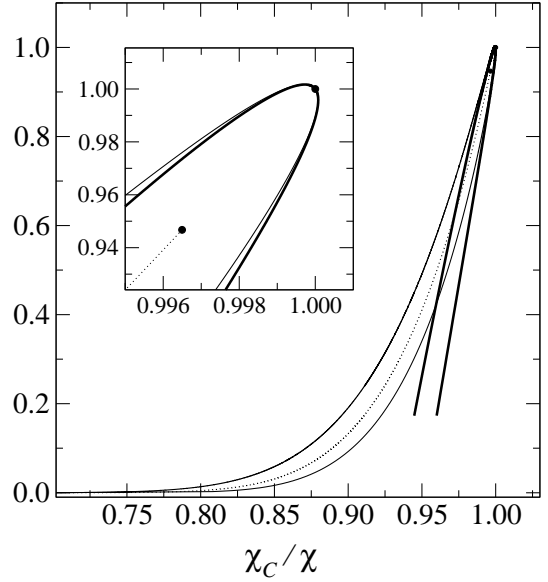


FIG. 2. $p-T$ phase diagram of the polymeric system described in the text. The thin line represents the exact numerical solution of the model, while the thick lines represent the Landau expansion. This curve shows exact first and second order derivatives at the critical point. The monodisperse limit is also shown (dotted line). Inset: Magnified view of the critical point.

Quantity	Landau Coefficients	Moments
α_{CL}	A_1, A_2	n_1, n_2, n_3
α_{SH}	A_1, A_2, B_1, B_2, C_0	n_1, n_2, n_3, n_4
β_{CL}	A_{1-4}, B_1, B_2, C_0	n_1, n_2, n_3, n_4
β_{SH}	$A_{1-4}, B_{1-4}, C_0, C_1, C_2, D_0$	n_1, n_2, n_3, n_4, n_5

TABLE I. Landau coefficients and moments needed to calculate slope and curvature parameters of the cloud and shadow.